(19) World Intellectual Property Organization International Bureau





(43) International Publication Date 20 November 2003 (20.11.2003)

PCT

(10) International Publication Number WO 03/095998 A1

(51) International Patent Classification⁷: G01N 25/72, 21/71

(21) International Application Number: PCT/BG02/00012

(22) International Filing Date: 26 June 2002 (26.06.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data: 106672 7 May 2002 (07.05.2002) BG

(71) Applicant (for all designated States except US): NAYDE-NOV, Jordan, Gueorguiev [BG/BG]; Blvd.Maritza No2, entr.11, app.44, 4000 Plovdiv (BG).

(71) Applicants and

(72) Inventors: DINEFF, Peter, Donchev [BG/BG]; h.k.Mladost 1, Bl.102, entr.M, app.208, 1797 Sofia (BG). STEFANOV, George, Stoyanov [BG/BG]; h.k.Mladost 4, Bl.428, entr.5, app.135, 1715 Sofia (BG).

(74) Agent: NEYKOV, Neyko, Hristov; 58, Vorino Str., app.2, 1680 Sofia (BG).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MA, MD, MK, MN, MW, MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SE, SG, SI, SK, TJ, TM, TN, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declaration under Rule 4.17:

of inventorship (Rule 4.17(iv)) for US only

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: METHOD FOR DETECTING AND IDENTIFICATION OF HAZARDOUS SUBSTANCE

(57) Abstract: The invention is related to a method for detection and identification of concealed substances or materials that are hazardous to humans and environment. The effective use of the method for detection and identification of hazardous substances, concealed by their inclusion in the masking matrix of various dielectric materials, is realized on the basis of the possibility of performing detection and identification of the hazardous substance in the matrix by means of the characteristic thermal picture of the material after thermal activating with a thermal pulse of defined geometrical parameters and energy, as said picture is an integral characteristic of the material ability to absorb the stimulating visible and infrared radiation and to transform it into a bulk or surface source of heat for the remaining part of the material, of the material ability to emit back the absorbed radiation, changing the wavelength of the incident radiation, and also of the material ability to perceive the absorbed thermal energy through thermal conductivity from the shaped-up secondary source of heat and to change its own temperature in that transitional thermal process.



WO 03/095998 PCT/BG02/00012

A METHOD FOR DETECTION AND IDENTIFICATION OF HAZARDOUS SUBSTANCES

FIELD OF THE INVENTION.

The invention is related to a method for detection and identification of concealed substances or materials that are hazardous to humans and environment. The hazardous substances may be diverse in their nature: explosive, inflammable, strongly toxic, biologically active or narcotic substances. Generally, such substances are concealed through their temporary or permanent inclusion into the matrix of various materials, for instance polymers, with the purpose of making an illegal transportation or use for a terrorist or other activity. Said materials are then used for making objects of traditional use, which impede their detection. Said method enables the fast and certain detection and identification of hazardous substances that have been concealed in that way.

BACKGROUND OF THE INVENTION.

25

30

The purposeful and most often malfeasant concealment of hazardous substances is performed through their temporary or permanent inclusion into a masking matrix of various materials. For instance, they are permanently included into the matrix of polymer materials, which are used for making objects of traditional use or processed materials in the form of powder, jelly, or shoe-cream. As concerns the temporary inclusion, it is most often realized into the microporous structure of a fabric or non-woven textile, first the material being immersed into a solvent, e. g. water, and then dried up. After the temporary inclusion into a microporous matrix, extracting said hazardous substance is performed through its dissolving anew in a solvent. Then said substance is extracted from the pores.

Hazardous substances may of different origin and diverse physical and chemical nature: explosive, inflammable, strongly toxic, biologically active or narcotic substances. Very often, in diverse production processes or as a result of consumption there occur substances being hazardous for humans and environment, which are not subject to a continuous safe storage, processing or use, but, at the same time, could be used ill-intentionedly through an appropriate concealment. Especially hazardous are toxic, strongly toxic, biologically active, narcotic, inflammable and explosive substances.

Explosive substances can be used in the form of the well known plastic explosive for in that concealed state they are always ready for use.

A lot of methods, based on various physical principles, for detection of hazardous explosive substances placed or concealed in metal casings (of electric conductivity) or in casings containing metal parts are known.

However, the main disadvantage of these methods known so far consists in their confined field of application, as they cannot be applied for detecting dielectric hazardous substances. Thus is important because that is the nature of the explosive substances and because that is the case of such substances concealed into a dielectrical masking matrix of no electric conductivity.

5

10

15

20

25

30

Methods of analysis are known, which are based on the fact that the hazardous substance, although concealed in an unusual form, is accessible by sampling the surface, for instance by means of an adhesive strip. Then the sample is examined by the highly sensitive nuclear magnetic resonance.

A primary disadvantage of the known method described above consists in its limited application because in the case of wetting (integrating) the hazardous substance from the matrix, e. g. an explosive substance, such a sample cannot be taken and examined. The same is valid for cases where an adhesive or similar substances of bonding properties are deposited on the material surface.

Methods for analysis of the structure and composition of dielectric materials are also known, which perform the analysis on particles dispersed over the surface or in the air or through their vapors emitted into the air. The analysis is performed at high treshold sensitivity (10 g/cm³) by means of detecting devices. To detect the concealed substance it is sufficient to bring the detecting device to a distance of 35 to 40 mm from the surface of examined body and move it at a speed of 40 mm/s over the examined surface. In these methods for detection and identification of a substance by its powder particles or vapors the principle of spectrometry is used, which is based on capturing the ion mobility of ionized vapors or particles of the substance.

The main disadvantage of said known method described above consists in its limited application, taking into consideration the fact that it is not efficient in detecting hazardous substances, which are wetted (integrated) and contained in the matrix of the fixing substance as well as in analyzing those substances, on the surface of which a special coating has been deposited with the purpose of not allowing the emission of powder or vapors into the air.

Methods for identification and analysis of the structure and composition of dielectric materials through electromagnetic polarization and depolarization of the polymer matrix as well as of the additives included into it are known. The analysis is carried out on the basis of the orienting action of the external force (magnetic or electric) field upon certain kinetic structural elements

WO 03/095998 3 PCT/BG02/00012

inherent to the matrix and filler: segments, groups, defects. The polarization (electrical or magnetic) of the dielectric is exhibited only in the presence of lightened kinetic mobility, i. e. upon its activation by heat or by introducing mechanic energy: through an acoustic action (ultrasound). Under these conditions, the orientation process of electrical or magnetic polarization is the primary one, while the physical structural modification of the material is the second aspect of manifestation of the polarized material. A characteristic structural anisotropy is exhibited as well as the anisotropy of the properties of the polarized material.

The electric polarization is realized at a relatively high intensity of the electric (permanentho or pulsed) field, which is hazardous for the service personnel and increases the risks of explosion or fire in case of accidentally occurrence of electric discharge in the air.

10

15

20

30

The magnetic polarization of diamagnetic type, i. e. that exhibiting the anisotropy transversely to the direction of the external magnetic field at relatively low induction of the magnetic field, is completely appropriate for characteristic modification of the properties of the diverse materials that contain a hazardous substance. The susceptibility of the kinetic structural elements to magnetic polarization depends on their relaxation nature, and also on the temperature-and-frequency regime of polarization. Every magnetically polarized body is anisotropic in its structure and properties. Every magnetically polarized body is electrically polarized, which leads to the exhibition of surface electric charge and of external electric field. Every magnetically polarized dielectric body can be studied either by examining its electric polarization, or by examining the forced anisotropy of its properties.

The forced change of the whole complex of physico-chemical properties due to the electromagnetic polarization can be used for identification not only of the polymer matrix, but also of the filling agent, namely the hazardous substance.

The measurement of the electric charge, electric potential and quantity of electricity provides an answer not only about the compositiona, but also even about the types and intensities of movement of in-25 dividual groups and segments. However, this type of analysis called a thermoelectretic analysis or method of the thermostimulated polarization and depolarization cannot be used under real conditions because it is realized slowly in thermodynamically balanced conditions (heating at a rate from 0.3 to 3.0 K/min, i. e. a "polarization - depolarization" analysis may go on for more than two hours. Moreover, this is carried out by using a specimen of the material in the form of a capacitor of dielectric thickness of 3 mm and diameter of at least 50 mm, or here the method in question is practically a destructive one, through which it will be possible to investigate the modification of materials or a technology for materials modification. This the main disadvantage that makes all existing methods using magnetic polarization non-applicable to detection and identification of hazardous substances in a masking matrix of common external shape.

A method for "visualization" of instantaneous two-dimensional invisible infrared image is known; a thermal picture that is periodically transformed into a visible image through the scanning linear movement of an elementary radiometric field of "vision" with an area many times smaller than that of the investigated picture, at which the distribution of the object's infrared brightness is transformed into visible brightness of the transformed image or into colour brightness corresponding to the infrared brightness of the visible image — a video signal that is received for decoding and visualization, the horizontal and vertical sweeps being synchronized with scanning in the surface analysis in such a way that the obtained thermal map of the surface reflect the relationship between the heat exchange realized through the thermal conductivity of the medium (the material) and its surface condition. Such systems are used not only in remote investigations of the Earth from the space, but also in the non-destructive testing of surfaces in respect to non-integrities: cracks, bubbles, cavities, etc. These methods have not been used for the detection and identification of substances hazardous for humans and environment, that have been concealed through their temporary or permanent inclusion in an appropriate masking matrix.

Infrared broadband radiometers with a planar focal zone and high resolution, for instance 256 × 256 pixels, could be also used for direct transformation of the invisible infrared picture of the surface into a visible image (in black and white or colours) for determining the surface and volumetric thermal state of such hazardous materials and objects.

SUMMARY OF THE INVENTION.

10

15

20

30

Having taken into consideration the known methods for detection or identification of hazardous substances described above, the purpose of present invention is to be created a method for detection and identification of hazardous substances concealed through their temporary or permanent inclusion into the masking matrix of diverse materials, of which objects of traditional use or processed materials in the form of powder, jelly or shoe-cream are made, said method being distinguished by increased technological and economical effectiveness, universality and reliability of detection and identification, improved quality and wider applicability.

The objective of the invention is achieved by a method for detection and identification of hazardous substances concealed through their temporary or permanent inclusion into a masking matrix of diverse materials, of which objects of traditional use or processed materials in the form of powder, jelly or shoe-cream are made.

The method for detection and identification of hazardous substances concealed through their temporary or permanent inclusion into a masking matrix of diverse materials, of which objects of traditional use or processed materials in the form of powder, jelly or shoe-cream are made, consists in subjecting a part of the material. i. e. a certain volume or layer located near the surface of the object or

material containing the concealed hazardous substance dispersed in its bulk, to an electromagnetic polarization, which, under the conditions of thermal or acoustical activation, depending on the intensity of the external magnetic field, apparent frequency of the external forced magnetic impact, composition and character of the material, causes an anisotropic re-structuring of the material in the direction along the external magnetic field or transversely to it, thus leading to the occurrence of a characteristic surface electric charge with a different sign and magnitude and a change in all physico-chemical bulk and surface properties of the polarized volume of the material, and in comparing the surface charge and its changed properties with the charge and properties of the remaining part of the bulk volume, unaffected by the polarization, and its adjacent surface of the material or object through "visualization", for instance by scanning the physical (electric or thermal) state of points from the whole surface, and transforming the magnitude of the electric charge or thermal potential into colour brightness of the image.

10

20

30

According to the invention, an external local thermal impact in the form of at least two separate identical spots of pre-set geometric form and average value of the surface density of the thermal power within 0.1 to 10.0 W/cm² is exerted upon an immobile or moving surface of the object or of the processed material, activating the group (and segment) kinetic molecular mobility of the hazardous substance and of masking matrix in the temperature range from room temperature (+15 °C ÷ +35 °C) to a temperature of 110 ÷ 120 °C, and an impact of a magnetic field perpendicular to the investigated surface with a maximum value of the magnetic induction within 0.05 to 0.8 T is exerted in the area of one of the two spots simultaneously with the thermal impact, a locally characteristic electromagnetic polarization of the material together with the concealed hazardous substance being performed in the area of one of the thermal spots, whereupon the thermal picture of the two thermal spots characterizing the material is periodically transformed into a visible image through scanning linear movement of an elementary radiometric field of "vision" with an area many times smaller than that of the investigated spots, upon which the distribution of the infrared brightness of the object is transformed into a visible brightness of the transformed image or into colours corresponding to the infrared brightness of the visible image - a video signal that is received for decoding and visualization, the horizontal and vertical sweeps being synchronized with scanning in the surface analysis in such a way that the obtained thermal map of the surface reflect the relationship between the heat exchange realized through the thermal conductivity of the medium (the material) and its composition and structure - once through expert comparison of the results obtained with representative results obtained preliminarily through consecutive comparison of materials with different contents of said hazardous substance, and again through immediate comparison of the heat exchanges in the two spots, i. e. in the absence or in the presence of a specific change in the structure of the masking matrix and hazardous substance under the effect of the magnetic field - through the

changes in the shapes and sizes of compared thermal spots after a known and precisely defined time period, through the difference between the maximum temperature values, and through the difference between the changes in the temperature gradient in different directions; and moreover: an analogous investigation of the invisible established two-dimensional picture of the distribution of the electrostatic charge on the surface of the two spots characterizing the material is performed in parallel with the investigation of the two-dimensional thermal picture, the magnitude of the electric charge being transformed into a visible image through the scanning linear movement of an elementary electromagnetic field of "vision" with an area many times smaller than that of the investigated spots, where the distribution of the magnitude of electric discharge is transformed into a visible brightness of the transformed image or 10 in colours corresponding to the magnitude of the surface electric charge - a video signal is obtained, which is received for decoding and visualization, the horizontal and vertical sweeps being synchronized with scanning in the surface analysis; - the so obtained map of surface distribution of the electric charge reflects the magnetic polarization of the masking matrix together with the hazardous substance in the area of the second spot, or the electric charge exhibits itself only in the area of the magnetically polarized material, the maximum value of the charge, its distribution, the change in the gradient of its distribution and the shape of observed spot being defined by the composition and structure of the material examined; and in such a way the presence and type of the hazardous substance are determined by applying expert examination and comparison of results obtained from the investigation of the thermal and electric pictures of the spots characterizing the material with representative results obtained preliminarily in the consecutive comparison of materials with different contents of said hazardous substance, and by directly comparing the thermal and electric characterizing spots obtained.

According to one embodiment of said method, the transformation of the invisible thermal image or thermal picture into visible image is realized by the scanning mechanical movement of an elementary radiometric field of "vision" with an area many times smaller than that of the examined spots, the horizontal and vertical image sweeps being synchronized with scanning in the surface analysis.

20

25

30

According to one embodiment of said method, the transformation of the invisible thermal image into visible image is realized directly by means of an infrared detector of three-dimensional resolution of at least 256 × 256 pixels and cryogenic cooling, excluding the use mechanic scanning system.

According to one embodiment of said method, the local thermal impact is realized upon the immobile surface of the object or material by a source of infrared thermal radiation, working in a pulsed regime in such a way that two identical round thermal spots of sufficiently large areas are formed by two consecutive pulses with the same geometric parameters and energy.

According to one embodiment of said method, the local thermal impact is realized upon the linearly moving surface of the object or material by two immobile sources of infrared thermal radiation, working in a continuous regime in such a way that parallel thermal stripes will be formed by the two identical focused spots when the surface is moving.

According to one embodiment of said method, the local thermal impact upon the linearly moving surface of the object or material is realized by one immobile linear source of infrared thermal radiation, working in a continuous regime in such a way that thermal spots in the form of parallel stripes along the direction of movement will be formed when the surface is moving.

According to another embodiment of said method, the local thermal impact upon the immobile surface of the object or material is realized by a mobile linear source of infrared thermal radiation, working in a pulsed regime in such a way that thermal spots in the form of two parallel stripes will be obtained transversally to the direction of movement when the source is moving.

10

20

25

According to another embodiment of said method, the local thermal impact upon the surface is realized by a focused pulsed emission of a source of coherent light radiation, a laser, with a wavelength in the visible or infrared light regions.

According to one embodiment of said method, the local thermal impact is realized by the focused emission of a linear or point bright infrared radiator (surface density of the radiator power within 50 to 58 W/cm², radiator temperature within 2300 to 2700 K), the shape of the spots being created by a thermal screen with appropriately formed openings for an immobile or moving surface of investigation.

According to another embodiment of said method, the local thermal impact is realized by the focused emission of a linear dark infrared radiator (surface density of the radiator power within 10 to 15 W/cm²), the shape of the spots being created by a thermal screen with appropriately formed openings for an immobile or moving surface of investigation.

According to another embodiment of said method, the local thermal impact is the result of an acoustic ultrasonic impact being realized at the location of pressing between investigated surface and the front part of an ultrasonic cylindrical tool of non-magnetic material as a result of acoustic losses at the point of mechanical contact at frequencies within 15 kHz to 40 kHz and surface density of the power within 0.2 go 0.4 W/cm².

According to one embodiment of said method, the magnetic field acts synchronously with the thermal impact during the formation of one of the spots and is created by a winding without any magnetic core, the axis of which is perpendicular to the investigated surface, the thermal impact being realized through its core.

According to another embodiment of said method, the magnetic field acting synchronously with the thermal impact during the formation of one of the spots is created by a permanent magnet in the shape of a hollow cylinder, the axis of which is perpendicular to the investigated surface, the thermal impact being realized through the core of the permanent magnet.

According to one embodiment of said method, the instantaneous two-dimensional invisible infrared image, i. e. the thermal map of the two thermal spots characterizing the material, is perceived during the transformation from the side of their formation, i. e. from the infrared thermal source.

According to another embodiment of said method, the instantaneous two-dimensional invisible infrared image, i. e. the thermal map of the two thermal spots characterizing the material, is also perceived through the bulk of the investigated material, more information about that part of the spectrum of the thermal visible and infrared radiations absorbed by the material being obtained during the expert examination and comparison of results obtained.

According to one embodiment of said method, only the results obtained from the investigation of the thermal map of the spots characterizing the material with representative results obtained preliminarily from a consecutive comparison of materials with different contents of the hazardous substance are subject to expert examination and comparison with the purpose of determining the presence and type of the hazardous substance.

10

20

25

According to another embodiment of said method, only the results from the direct comparison of the obtained thermal characterizing spots are subject to expert examination and comparison with the purpose of determining the presence and type of the hazardous substance.

According to another embodiment of said method, only the results obtained from the investigation of the electric picture of the spots characterizing the material are subject to expert examination and comparison with the purpose of determining the presence and type of the hazardous substance.

According to one more embodiment of said method, the expert examination and comparison are performed by computerized information processing and a unitary estimate of the presence and type of the hazardous substance is presented.

The effective use of the method for detection and identification of hazardous substances, concealed by their inclusion in the masking matrix of various dielectric materials, is realized on the basis of the possibility of performing detection and identification of the hazardous substance in the matrix by means of the characteristic thermal picture of the material after thermal activating with a thermal pulse of defined geometrical parameters and energy, as said picture is an integral characteristic of the material ability to absorb the stimulating visible and infrared radiation and to transform it into a bulk or surface source of heat for the remaining part of the material, of the material ability to emit back the absorbed radiation, changing the wavelength of the incident radiation, and also of the material ability to perceive the absorbed thermal energy through thermal conductivity from the shaped-up secondary source of heat and to change its own temperature in that transitional thermal process.

The comparison is carried out on the basis of a database for the thermal picture of standard samples from various materials with different volumetric or mass contents of the hazardous substance; the suc-

cessful detection and identification of concealed hazardous substances will require an enormous volume of preliminary investigations and the creation of an expert system for making decisions. The system should be subject to self-instruction in the process of its use.

Using said method creates conditions and possibilities for detection and identification of a hazardous substance by the thermal picture of the magnetically polarized material that carries more additional information about the composition and structure of the composite material by the modified initial shape of the thermal spot, as in this case the change towards anisotropy in the thermal properties of the material in the area of thermomagnetic treatment is also involved, i. e. the modified shape from an initially round spot towards an oval with a longer or shorter transversal axis is determined by the exhibited anisotropy. All this carries more additional information about the composition and changes in the structure of the composite material.

5

15

20

The detection and identification of the hazardous substance are carried out by comparison on the basis of a database for the thermal picture of standard samples from various materials with different volumetric or mass contents of the hazardous substance.

Applying said method makes available the possibility of a comparative examination of the shape and distribution of the colour brightness of the two spots: in the zone of thermal and thermomagnetic external impact, including also by superposition (addition or subtraction) of the two pictures: a differential comparison.

The detection and identification of the hazardous substance are carried out by a differential comparison on the basis of a database for the thermal pictures of standard samples from various materials with different volumetric or mass contents of the hazardous substance.

It is possible to visualize the distribution picture for the electrostatic charge or the electric potential in the region of the two spots and to analyse it by differential superposition.

The detection and identification of the hazardous substance are carried out by differential comparison on the basis of a database for the electrical pictures of standard samples from various materials with different volumetric or mass contents of the hazardous substance.

Possibilities are created for using all measurements according to the schemes indicated earlier and for performing the detection and identification on the basis of all acquired data. It will be rational to perform the detection and identification by stages: if the investigation of the first spot gives a positive answer, investigating the second spot will be obligatory, as it will give an irrefutable evidence for the composition and structure of the composite hazardous material, but the remaining two stages could be avoided in order not to lengthen the time necessary for processing the information. However, when the answer is negative, it will be such just in the case of performing all the four stages, which corresponds to the maximum degree of certainty in decision making. It is possible, of course, to carry out thermal

WO 03/095998 10 PCT/BG02/00012

investigations only, which will simplify the method but will by no means make the decision taken more reliable.

The detection and identification of the hazardous substance are carried out on the basis of all data (from the thermal and electrical pictures) from the investigation, performing a comparison with standard samples from various materials with different volumetric or mass contents of the hazardous substance. The successful detection and identification of concealed hazardous substances will require preliminary investigations and the creation an expert system for making decision. The system should be subject to self-instruction in the process of its use.

DETAIL DESCRIPTION OF THE INVENTION

10

15

20

25

The method according to the invention can be applied to detecting and identifying substances, hazardous for humans and the environment (toxic, strongly toxic, biologically active, explosive, inflammable), that have been purposefully concealed through their temporary or permanent inclusion in the masking matrix of various dielectric materials, of which objects of traditional use or processed materials in the form of powder, jelly or shoe-cream are made.

Said method is realized in-the following sequence: initially, an infrared pulse source of heat is directed towards the immobile surface of the processed material – a thermoreactive matrix with an explosive substance as a filler, included as 75 percent of the mass - and two thermal spots of identical geometry, situated next to each other, are formed, where in the formation of the second spot the infrared light beam goes through the core of a small winding that creates a pulsed magnetic field and polarizes the magnetically activated composite material. The surface density of the power in focused thermal spot is of the order of 4 W/cm². The background temperature in the thermally (dark) insulated investigation chamber is 20 °C (about 293 K).

The maximum value of magnetic induction in the area of the second thermal spot is 0.11 T. The magnetic pulse is synchronized with certain accuracy with the thermal radiation form the source in the area of the second spot. The two spots are observed for one minute at intervals of 10 s, the thermal picture being taken several times by means of an infrared camera for non-destructive testing.

The thermal picture is perceived from the side of the incident infrared beam. There follows a comparative analysis of thermal pictures, which is performed by the shape of the spots and its change with time, the distribution of the colour brightness over the section of the spots and the anisotropy of the second spot. The detection and identification are carried out by expert analysis of the database from an experimental investigation of standard samples from the base of the same matrix with different content of the hazardous substance.

Said method can be illustrated by the following exemplary embodiments:

WO 03/095998 11 PCT/BG02/00012

Example 1.

10

15

20

25

30

Two test specimens are used: •a mail envelope containing an elastic explosive substance (an experimental elastic explosive substance on the basis of tetranitrocentaerythrit - TEN835) in the form of a sheet with a thickness of 0.7 mm and •a mail envelope containing paper sheets. The envelopes are sealed and of the same exterior.

A harmonically changing infrared radiation with frequency 0.03 Hz (mechanical modulation) from a powerful halogen lamp (1 kW) is used for exerting an impact on the whole surface of the mail envelope. A thermal wave is propagated through the material medium and penetrates to a depth μ that depends on the thermal conductivity λ , mass density ρ and thermal capacity c, i. e. on the thermal properties of

materials as well as on the frequency of modulation $\omega = 2\pi f$: $\mu = \sqrt{\frac{2\lambda}{\omega \rho c}} = \sqrt{\frac{2a}{\omega}}$. The thermal wave is reflected by the non-integrities and forms a backward thermal radiation that is perceived by an camera. This way two images are formed: one corresponding to the magnitude, which indicates the differences between the bodies concealed in the mail envelope, and another corresponding to the phase that is characteristic for the material.

A magnetic field of induction 0.11 T is used for exerting an impact on a part of the heated surface (a 15-mm wide stripe is obtained by moving the envelope), which causes a magnetic polarization not only of the envelope material, but also of its content. The electrostatic charge of the surface (by using an electrometer) or the intensity of the electric field (resulting from the polarization of materials) is measured immediately.

In such a way three essential (characteristic) differences are obtained, which are used for the identification: first, a picture of the envelope interior that shows the different content (the material is not identified!); second, a phase picture being a characteristic of the material, which is used for its identification by comparison with preliminarily prepared standards; and third, a high electric potential or large electrostatic charge, which is characteristic for the elastic explosive. These three differences allow the detection of the plastic explosive by the form (if there is any difference) and by two different integral characteristics: a thermal and electric ones.

Example 2.

The same test specimens are used (mail envelopes with different contents). The surface of each envelope is subject twice to a single and continuous impact with an infrared (thermal) package of pulses – mechanically modulated light from a ruby laser – similarly to the modulation of Example 1. Two round spots are formed on the investigated surface, the second being formed during the additional impact of the magnetic field with induction 86 mT, acting in parallel to the surface.

An infrared camera is used for observation of the change occurring in the spots with time – a change in the colour picture, i. e. in the temperature distribution, and a deviation from the round shape. An anisotropy of the thermal properties results from the magnetic polarization, which is reflected in the formation of a spot with the shape of an ellipse.

The electric charge emerging on the envelope surface and the intensity of the electric field (resulting from the magnetic polarization) are also measured.

Two essential differences are obtained, which are used for detecting the content: first, a different temperature picture of the spot that is characteristic for the material inside the envelop, and second, a deviation in spot geometry which is characteristic for the magnetic polarization are of the envelope material and of the sheet inside it.

Example 3.

5

10

15

30

Two test specimens are checked: the first one, a metal vial, by shape and external design (inscriptions, graphical images) is identical to the second vial and is filled with an irritating and tear-exciting toxic combat substance from the group of chlorine agents: chloracetonephenone (CN); the second one contains a shaving foam, which is a content corresponding to the label.

The procedure is according to that described in Example 1, the modulation frequency being chosen such that the thermal wave will penetrate deeply into the content of the metal vial: a frequency of 0.3 Hz.

Two essential and characteristic differences are obtained, which are used for identification: first, a picture of the vial interior that will indicate the different content (the material is nor identified!); and second, a phase picture that is a characteristic of the material and is used for its identification by comparison with preliminarily prepared standards. These two differences allow the detection of the toxic combat substance.

Example 4.

This inspection uses the specimens of Example 3.

The surface of each vial is subject twice to a single and continuous impact with an infrared (thermal) package of pulses – mechanically modulated light from a ruby laser similarly to the modulation of Example 1. Two round spots are formed on the investigated surface, the second one being formed by the additional impact of a magnetic field with induction of 60 mT acting in parallel to the surface.

An infrared camera is used for the observation of the change occurring in the spots with time: a change in the colour picture, i. e. of the temperature distribution, and a deviation from the round shape. An anisotropy of thermal properties results from the magnetic polarization, which is reflected in the formation of a spot with the shape of an ellipse. Two essential differences are obtained, which are used for detecting the content: the first one is a different temperature picture of the spot that is characteristic

for the material inside the vial, and the second one is a deviation in the spot geometry that is characteristic for the magnetic polarization of the material inside the vial.

5 Example 5.

, ;

Two glass packages are checked: one containing a strong inflammable substance (napalm) in jelly-like form, and the other containing a jelly made of strawberries. Both glass packages have the same external appearance corresponding to the content of strawberry jelly.

The inspection is performed in accordance with the method described in Example 1.

10 Example 6.

The glass packages of Example 5 are checked.

The inspection is realized in accordance with the method described in Example 2.

Example 7.

Two specimens are checked: parts of a metal walking stick, one of these is made of an aluminum alloy, and the other of a strong inflammable alloy of aluminum and magnesium called electron. Both specimens have the same form (a cylinder), and the difference by colour and brightness between them is not considerable.

The inspection is performed in accordance with the methodology described in Example 1 with the difference that in this case the electric potential or electrostatic charge is not measured. The picture of the temperature field and the phase picture are completely sufficient for detecting the difference between the two materials.

15

20

WO 03/095998 14 PCT/BG02/00012

Claims

, 1

5

10

15

20

25

30

35

1. A method for detection and identification of substances hazardous for humans and the environment, being concealed through their temporary or permanent inclusion into the masking matrix of various materials, from which objects of traditional use or processed materials in the form of powder, jelly or shoe-cream are made, said method being characterized by the fact that a local thermal impact in the form of two separate identical spots with a pre-set geometric shape and an average value of surface density of the thermal power within 0.1 to 10.0 W/cm² is exerted upon the immobile or moving surface of said object or of said processed material, said impact activating the group (and segment) kinetic molecular mobility of the hazardous substance and of the masking matrix in the temperature range from room temperature (+15 $^{\circ}$ C ÷ +35 $^{\circ}$ C) to a temperature of 110 ÷ 120 $^{\circ}$ C, and that also a magnetic field, which is normal (perpendicular) to the investigated surface with a maximum value of the magnetic induction within 0.05 to 0.8 T, exerts an impact in the area of one of the two spots simultaneously with the thermal impact that activates the kinetic mobility, whereupon the instantaneous two-dimensional invisible infrared image (the thermal picture) of the two thermal spots characterizing the material is transformed into a visible image through the scanning linear movement of an elementary field of "vision" with an area many times smaller than that of the investigated spots, upon which the distribution of the infrared brightness of the object is transformed into a visible brightness of the transformed image or into colours corresponding to the infrared brightness of the visible image – a video signal that is received for decoding and visualization, the horizontal and vertical sweeps being synchronized with scanning in the surface analysis in such a way that the obtained thermal map of the surface reflect the relationship between the heat exchange realized through the thermal conductivity of the medium (the material) and its composition and structure - once through expert comparison of the results obtained with representative results obtained preliminarily through consecutive comparison of materials with different contents of said hazardous substance, and again through immediate comparison of the heat exchanges in the two spots, i. e. in the absence or in the presence of a specific change in the structure of the masking matrix and hazardous substance under the effect of the magnetic field - through the changes in the shapes and sizes of compared thermal spots after a known and precisely defined time period, through the difference between the maximum temperature values, and through the difference between the changes in the temperature gradient in different directions; and moreover: an analogous investigation of the invisible established two-dimensional distribution picture of the electrostatic charge on the surface of the two spots characterizing the material is performed in parallel with the investigation of the two-dimensional thermal picture, the magnitude of the electric charge being transformed into a visible image through the scanning linear movement of an elementary electromagnetic field of "vision" with an area many times smaller than that of the investigated spots, where the distribution of the magnitude of electric discharge is transformed into a visible brightness of the transformed image or in colours corresponding to the magnitude of the surface electric

charge - a video signal is obtained, which is received for decoding and visualization, the horizontal and vertical sweeps being synchronized with scanning in the surface analysis; - the so obtained map of surface distribution of the electric charge reflects the magnetic polarization of the masking matrix together with the hazardous substance in the area of the second spot, or the electric charge exhibits itself only in the area of the magnetically polarized material, the maximum value of the charge, its distribution, the change in the gradient of its distribution and the shape of observed spot being defined by the composition and structure of the material examined; and in such a way the presence and type of the hazardous substance are determined by applying expert examination and comparison of results obtained from the investigation of the thermal and electric pictures of the spots characterizing the material with representative results obtained preliminarily in the consecutive comparison of materials with different contents of said hazardous substance, and by directly comparing the thermal and electric characterizing spots obtained.

2. A method according to claim 1, characterized by the fact that the local thermal impact

5

10

20

25

upon the immobile surface of the object or material is realized by a source of (infrared) thermal radiation, working in a pulsed regime in such a way that two identical round thermal spots are formed by two consecutive pulses with the same energy;

3. A method according to claim 1, characterized by the fact that tocal thermal impact upon

the linearly moving surface of the object or material is realized by two immobile sources of (infrared) thermal radiation, working in a continuous regime in such a way that parallel thermal stripes will be formed by the two identical focused spots when the surface is moving;

- 4. A method according to claim 1, characterized by the fact that the local thermal impact upon the linearly moving surface of the object or material is realized by an immobile linear source of (infrared) thermal radiation, working in a pulsed regime in such a way that thermal spots in the form of two parallel stripes will be obtained transversally to the direction of movement when the surface is moving;
- 5. A method according to claim 1, characterized by the fact that the local thermal impact upon the immobile surface of the object or material is realized by a mobile linear source of (infrared) thermal radiation, working in a pulsed regime in such a way that thermal spots in the form of two parallel stripes will be obtained transversally to the direction of movement when the source is moving;

WO 03/095998 16 PCT/BG02/00012

, •

5

15

20

25

6. A method according to claim 1, characterized by the fact that the local thermal impact upon the surface is realized by a focused pulsed emission of a source of coherent light radiation, a laser, with a wavelength in the infrared light region;

- 7. A method according to claim 1, characterized by the fact that the local thermal impact is realized by the focused emission of a linear or point bright infrared radiator (surface density of the radiator power within 50 to 58 W/cm², radiator temperature within 2300 to 2700 K), the shape of the spots being created by a mask: a thermal screen with appropriately formed openings for an immobile or moving surface of investigation;
- 8. A method according to claim 1, characterized by the fact that the local thermal impact is realized by the focused emission of a linear dark infrared radiator (surface density of the radiator power within 10 to 15 W/cm²), the shape of the spots being created by a mask: a thermal screen with appropriately formed openings for an immobile or moving surface of investigation;
 - 9. A method according to claim 1, characterized by the fact that said local thermal impact is a result of an acoustic, i. e. ultrasonic impact being realized in the location of pressing between the investigated surface and the front part of an ultrasonic cylindrical tool of non-magnetic material (for instance, duralumin) as a result of acoustic losses at the point of mechanical contact at frequency within 15 kHz to 40 kHz and surface power density within 0.2 to 0.4 W/cm²;
 - 10. A method according to claim 1, characterized by the fact that said magnetic field acts synchronously with said thermal impact during the formation of one of said spots and is created by a winding without any magnetic core, the axis of which is perpendicular to the examined surface, said thermal impact being realized through its core;
 - 11. A method according to claim 1, characterized by the fact that said magnetic field acts synchronously with said thermal impact during the formation of one of said spots and is created by a permanent magnet having the shape of a hollow cylinder, the axis of which is perpendicular to the examined surface, said thermal impact being realized through the core of said permanent magnet;
 - 12. A method according to claim 1, characterized by the fact that said instant two-dimensional invisible infrared image, i. e. the thermal map of said two thermal spots characterizing said material, is perceived in the transformation from the side of their formation or from said infrared thermal source;
- 13. A method according to claim 12, characterized by the fact that said instant two-dimensional invisible infrared image, i. e. the thermal map of said two thermal spots characterizing said material, is

perceived in the transformation through the bulk of the examined material as well, and that more information about that part of the spectrum of the (thermal) infrared radiation, which is absorbed by the material, is obtained by expert examination and comparison of results obtained.

14. A method according to claim 1, characterized by the fact that solely the results obtained by the examination of the thermal map of said spots characterizing said material with representative results obtained preliminarily by consecutive comparison of materials having diverse contents of said hazardous substance are subject to expert examination and comparison with the purpose of determining the presence and type of said hazardous substance;

5

- 15. A method according to claim 1, characterized by the fact that solely the results from the direct comparison of obtained thermally characterizing spots are subject to expert examination and comparison with the purpose of determining the presence and type of said hazardous substance;
 - 16. A method according to claim 1, characterized by the fact that solely the results obtained by examining the electric picture of said spots that characterize said material are subject to expert examination and comparison with the purpose of determining the presence and type of said hazardous substance;
 - 15 17. A method according to claim 1, characterized by the fact that the expert examination and comparison are realized by computerized information processing and a unitary estimate of the presence and type of said hazardous substance is presented.

INTERNATIONAL SEARCH REPORT

Internatil Application No PCT/BG 02/00012

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 G01N25/72 G01N21/71

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols) $IPC\ 7\ G01N$

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUM	ENTS CONSIDERED TO BE RELEVANT	
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Υ	US 4 578 584 A (BAUMANN THOMAS ET AL) 25 March 1986 (1986-03-25)	14,15
A	column 4, line 14 - line 60 column 7, line 22 -column 8, line 36; figure 2	1,2,17
Υ	US 4 679 946 A (ROSENCWAIG ALLAN ET AL) 14 July 1987 (1987-07-14)	14,15
Α	column 4, line 34 -column 5, line 31; figure 2	1-3,6
Υ	WO 87 00632 A (KANOR AS) 29 January 1987 (1987-01-29)	14,15
Α	page 18, line 5 -page 19, paragraph 3; figures 1,2,9-12	1
	-/	

X Further documents are listed in the continuation of box C.	χ Patent family members are listed in annex.
Special categories of cited documents: 'A' document defining the general state of the art which is not considered to be of particular relevance 'E' earlier document but published on or after the International filing date 'L' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) 'O' document referring to an oral disclosure, use, exhibition or other means 'P' document published prior to the International filing date but later than the priority date claimed	 *T* later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. *&* document member of the same patent family
Date of the actual completion of the International search 30 January 2003	Date of mailing of the international search report 12/02/2003
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentiaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Stuebner, B

INTERNATIONAL SEARCH REPORT

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

Internat Application No PCT/BG 02/00012

		PCT/BG 02/00012
	ation) DOCUMENTS CONSIDERED TO BE RELEVANT	
Category °	Citation of document, with Indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 839 913 A (ANNIS MARTIN ET AL) 13 June 1989 (1989-06-13) column 3, line 1 -column 4, line 54; figures 1,5	1,14-16
A	US 3 997 787 A (FEARON ROBERT E ET AL) 14 December 1976 (1976-12-14) column 2, line 15 - line 55	1,14-16
A	US 5 228 776 A (SMITH WALTER L ET AL) 20 July 1993 (1993-07-20) abstract column 5, line 10 -column 6, line 9; figures 3-5	1,9, 14-16
A	US 6 183 126 B1 (MURPHY JOHN C ET AL) 6 February 2001 (2001-02-06) column 1, line 15 - line 62; figures 1,2	9
i		
!		
		·
		·

INTERNATIONAL SEARON REPORT

Information on patent family members

Internati Application No PCT/BG 02/00012

Patent document Publication cited in search report date			Patent family		Publication		
			date	member(s)		date	
US	4578584	Α	25-03-1986	DE	3485576	D1	16-04-1992
				EP	0150384	A2	07-08-1985
				JP	60154224	A	13-08-1985
US	4679946	A	14-07-1987	DE	3579497	D1	11-10-1990
				EP	0163466	A2	04-12-1985
				JP	1948624		10-07-1995
				JP	6084942	_	26-10-1994
				JP	60256038	Α	17-12-1985
WO	8700632	Α	29-01-1987	NO	852833	Α	16-01-1987
				AU	6135786		10-02-1987
				BR	8606794		13-10-1987
				CN	86105818		10-06-1987
				DK	130087		13-03-1987
				EP	0229816		29-07-1987
				FI	871117		13-03-1987
				JP	63500336		04-02-1988
				WO	8700632		29-01-1987
US	4839913	Α	13-06-1989	NONE			
US	3997787	 A	14-12-1976	CA	1041679	A1	31-10-1978
				GB	1550887	A	22-08-1979
US	5228776	Α	20-07-1993	NONE			
115	6183126	B1	06-02-2001	US	2001007571	 Λ1	12-07-2001